

CCA-664

530.145:541

Note

A New Form of the Two-Center Integral and its Application in the Semiempirical LCAO MO Method

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Received April 4, 1971

The value of the two-center Coulomb integral

$$\langle ii | jj \rangle = \int |\Phi_i(r_1)|^2 \frac{1}{r_{12}} |\Phi_j(r_2)|^2 dr_1 dr_2$$

are of great importance in the semiempirical LCAO MO methods, *e.g.* in the P—P—P¹ one. When $i=j$, the empirical value about 11 eV was introduced instead of the value 16.9 eV calculated with Slater orbitals. This reduction was interpreted as a readjustment of σ electrons which then »screen« the Coulomb interaction. A similar correction has been applied to the two-center integral by Pariser and Parr² with the polynomial interpolation formula or with a form suggested by Nishimoto and Mataga³.

In recent time it became clear that in large molecular systems the two-center Coulomb integral has to be corrected because of the screening between π electrons themselves. Little⁴ calculated this screening using a point test charge model⁵ in the static limit which is a valid procedure for low lying excitations.

The aim of this work is to show that one can introduce a simple »screened« Coulomb potential which agrees with that calculated by Little. The potential of the form

$$V(1, 2) = \frac{1}{r_{12}} (1 - \exp(-\beta r_{12})) \quad (1)$$

was introduced by McWeeny⁶ on the following arguments: $V(1, 2)$ has a finite value β at $r_{12} \rightarrow 0$, but decreases to zero with $r_{12} \rightarrow \infty$. This finite value at $r_{12} \rightarrow 0$ is important for electrons with antiparallel spins. The potential (1) introduces in a semiempirical manner a correlation effect. Two-center integrals with potential (1) were calculated using Slater 2p atomic orbitals (Appendix). The constant β in potential (1) is a semiempirical parameter and was determined by the values $V(1, 2)$ at the same atomic site ($i=j$). The values of these integrals were taken 10.53 eV (ref. 2) and 11.7 (ref. 3) eV, respectively.

The $V(1, 2)$ potential of Mataga-Nishimoto, Little and ours are shown in Fig. 1. In the studied region the potential (1) agrees better with that of Little than with Mataga-Nishimoto's one. There are of course differences between both of them: i) potential (1) decreases faster to zero than Little's one ii) potential (1) is space independent while Little's is space dependent.

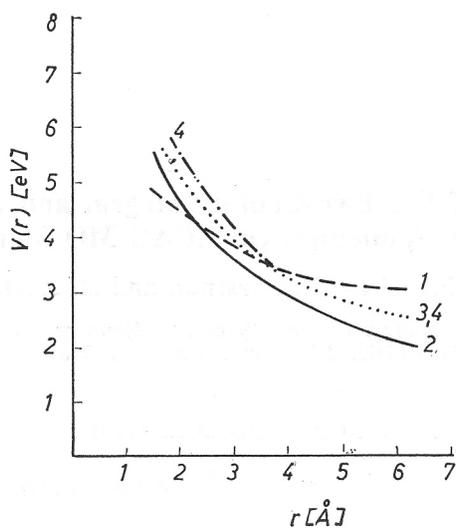


Fig. 1. (1) Screened potential (ref. 1), (2) Mataga-Nishimoto potential, (3) Potential eq. 1/(ii/ii) = 10.53 eV, (4) Potential eq. 1/(ii/ii) = 11.70 eV.

Little tested his potential with the calculation of the excitations in two large conjugated systems: hexabenzocorone and coronene. We did the same type of calculation with the following assumption: all bond lengths are equal to 1.41 Å, one-center integrals have values 10.53 eV and resonance integrals 2.3 eV. Sixteen configurations were considered in the configuration-interaction method. In Fig. 2 we compared three computations with potential Mataga-Nishimoto, potential (1), and with Little's one. The calculation with

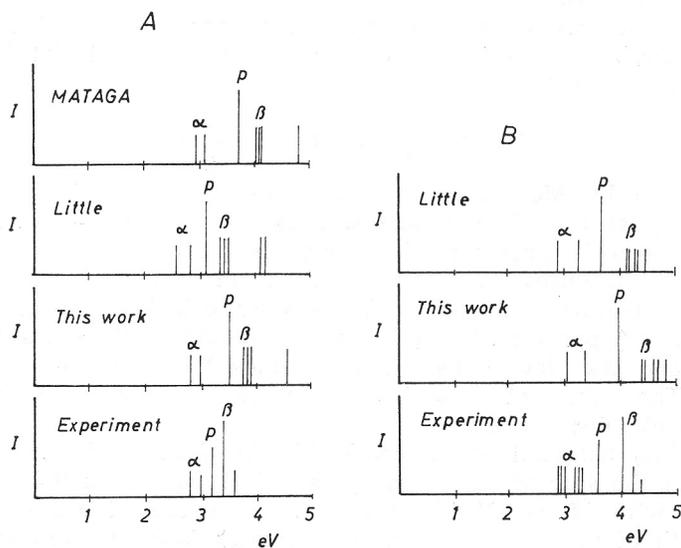


Fig. 2. Calculated spectrum: (A) hexabenzocorone, (B) coronene.

potential (1) gives a very good agreement with experiment. This of course is not surprising. Little's screened potential and the potential (1) are quite close to one another at larger distances. The calculation of low energy excitations just depends more strongly on these distances than on small ones.

Potential (1) can be quite powerful for the calculation in large molecular systems and gives better agreement with experiment than other proposed potentials. We did not study the application of potential (1) to the calculation of high energy excitations. We do not know if this potential fail in this region as Little's does.

APPENDIX

The Coulomb two-center integral has the form

$$F(\gamma, \beta, R) = R \iint \Phi_1^2(\vec{a} - \vec{r}_1) \frac{1 - \exp[-\beta(|\vec{r}_1 - \vec{r}_2|)]}{|\vec{r}_1 - \vec{r}_2|} \Phi_2^2(\vec{r}_2 - \vec{b}) d\vec{r}_1 d\vec{r}_2$$

where Φ_1 is the Slater 2 p atomic orbital, γ Slater parameter and $\vec{R} = \vec{a} - \vec{b}$. F can be written as

$$F(m, n) = G(m, 0) - G(m, n)$$

with the symbols $m = \gamma R$ and $n = \beta R$

$$G(m, n) = R \int \Phi(\vec{a} - \vec{r}_1) \Psi(\vec{r}_1 - \vec{r}_2) \Phi(\vec{r}_2 - \vec{b}) d\vec{r}_1 d\vec{r}_2$$

where

$$\Psi(\vec{r}) = \exp(-\beta r)/r; \quad \Phi(\vec{r}) = \Phi_1^2(\vec{r})$$

To calculate F we first evaluate G. The parameters ρ and r were introduced as $\vec{r}_1 = \vec{b} + \vec{r}$ and $\vec{r}_2 = \vec{b} + \vec{\rho}$ and G takes the form

$$G = R \int \Phi(\vec{R} - \vec{r}) d\vec{r} \int \Psi(\vec{r} - \vec{\rho}) \Phi(\vec{\rho}) d\vec{\rho}$$

With the notation

$$g(\vec{r}) = \int \Psi(\vec{r} - \vec{\rho}) \Phi(\vec{\rho}) d\vec{\rho}$$

G obtained a compact form

$$G = R \int g(\vec{r}) \Phi(\vec{R} - \vec{r}) d\vec{r}$$

Fourier transform of G is

$$\vec{G}(\vec{k}) = R \cdot \vec{g}(\vec{k}) \vec{\Phi}(\vec{k}) = R [\vec{\Phi}(\vec{k})]^2 \vec{\Psi}(\vec{k})$$

Fourier transforms $\vec{\Phi}$ and $\vec{\Psi}$ were calculated analytically. G was evaluated using the inverse Fourier transformation:

$$G = (2\pi)^{-3} \int \exp(-i\vec{k}\vec{r}) \cdot \vec{G}(\vec{k}) d\vec{k}$$

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IZVLEČEK

Dvocentrični integral in njegova uporaba v semiempirični LCAO MO metodi

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Predpostavljen je potencial, ki na semiempirični način upošteva korelacijo med elektroni. LCAO MO metoda s dvocentričnimi integrali izračunanimi s tako predpostavljenim potencialom, da boljše ujemanje z eksperimentom kot s ostalimi načini izračunani integrali.

KEMIČNI INŠTITUT »BORIS KIDRIČ«

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ODDELEK ZA KEMIJO
 UNIVERZE V LJUBLJANI

Sprejeto 4. aprila 1971.